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(54) [Title of the Invention]

Biodegradable Film

(57) [Summary]

[Object] The present invention relates to providing a biodegradable film that solves blocking problems.

[Means of Achievement] The present invention provides a biodegradable film containing two or more components selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also containing an inorganic filler and an ethylene/vinyl acetate copolymer. The composition may also contain as required one or more components selected from thermal stabilizers, plasticizers, lubricants, and modified silicones.

[Claims]

[Claim 1] A biodegradable film containing two or more components selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also containing an inorganic filler and an ethylene/vinyl acetate copolymer.

[Claim 2] A biodegradable film containing a composition composed of one or more components selected from thermal stabilizers, plasticizers, lubricants, and modified silicones added to a composition containing two or more components selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also containing an inorganic filler and an ethylene/vinyl acetate copolymer

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a biodegradable film, and more specifically to a biodegradable film that prevents blocking.

[0002]

[Prior Art] Biodegradable films have recently come into production, but when film produced by T-die extrusion, drawing, or another method is wound in several layers and left to stand, the film layers adhere to each other and become difficult to separate when used, often causing problems in practical terms.

[0003]

[Problems to Be Solved by the Invention] The present invention relates to a biodegradable film in which the blocking problem has been overcome.

[0004]

[Means Used to Solve the Above-Mentioned Problems] The present inventors, as a result of thoroughgoing research, discovered that it is possible to provide a biodegradable film containing two or more biodegradable polymers selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also containing an inorganic filler and an ethylene/vinyl acetate copolymer. The composition may also contain as required one or more components selected from thermal stabilizers, plasticizers, lubricants, and modified silicones.

[0005] More specifically, the present invention successfully prevents mutual film blocking by adding a certain type of inorganic filler. The film naturally decomposes if left in soil or salt water after being used, and is therefore effective from the aspect of environmental protection.

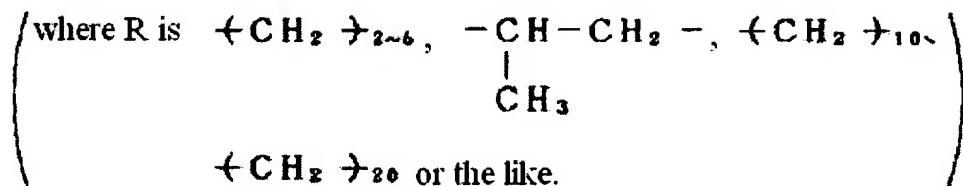
[0006]

[Embodiments of the Invention] In the present invention, a lactic acid polymer is used as the biodegradable polymer, and included therein are polylactic acids, lactic acid/hydroxyl carboxylic acid copolymers, and the like. The polylactic acid used in the present invention is one obtained by subjecting L-lactic acid, D-lactic acid, or a mixture thereof to dehydrocondensation, and is preferably one obtained by subjecting a lactide (which is a cyclic dimer of lactic acid) to ring-opening polymerization. Lactides include L-lactide (cyclic dimer of L-lactic acid), D-lactide (cyclic dimer of D-lactic acid), meso-lactides in which D- and L-lactic acid have been subjected to cyclic dimerization, and DL-lactides (which are mixtures of D- and L-lactides), and are obtained by subjecting one or more of the above to ring-opening polymerization. The ring opening polymerization of lactide is preferred since the lactide is easy to polymerize, and a product with a higher degree of polymerization can be readily obtained. The weight-average molecular weight of the polylactic acid used in the present invention is not particularly limited but is ordinarily in the range of 30,000 to 1,000,000, is preferably 100,000 to 300,000. Commercially available examples of polylactic acids include ECOPLA (manufactured by Cargill) and LACTY (manufactured by Shimadzu).

[0007] Examples of the copolymer of lactic acid and hydroxyl carboxylic acid used in the present invention include lactic acid/glycolic acid copolymers and the like, and the molar ratio of lactic acid units is 50 molar percent or higher, and is preferably 80 molar percent or higher. This is due to the fact that if the molar ratio of lactic acid units is less than 50 molar percent, the breaking strength and biodegradation rate are reduced. The weight-average molecular weight of the copolymer of lactic acid and hydroxyl carboxylic acid is in a range of 5,000 to 250,000. This is due to the fact that if the weight-average molecular weight is less than 5,000, satisfactory elongation at break cannot be obtained, and if the weight-average molecular weight exceeds 250,000, the breaking strength will be reduced.

[0008] The glycol/aliphatic dicarboxylic acid copolymer (which is one of the biodegradable polymers used in the present invention) is aliphatic polyester synthesized by polycondensation of glycol and aliphatic dicarboxylic acid, and the glycol is expressed by the following formula.

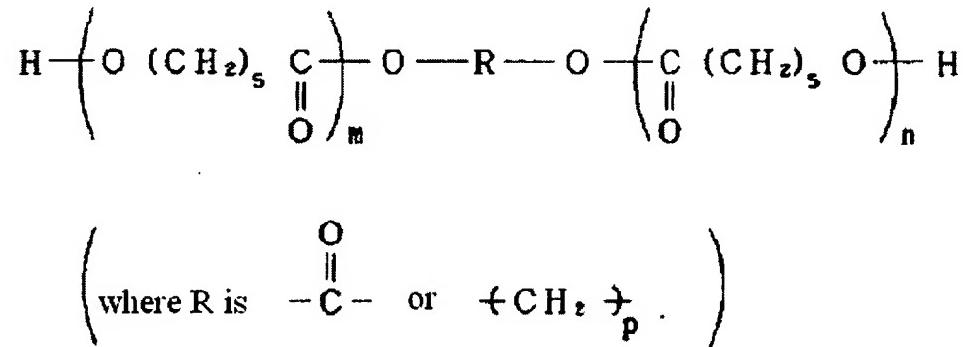
[Chemical Formula 1]



The aliphatic dicarboxylic acid is expressed by the formula HOOC (CH₂)_k COOH, where *k* is a value between 0 and 8. If *k* is 9 or higher, reactivity is reduced and polymerization becomes difficult. The weight-average molecular weight of the glycol/aliphatic dicarboxylic acid copolymer is 10,000 to 200,000, and is preferably in a range of 50,000 to 100,000. The glycol content is 20 to 70 % by weight, and the aliphatic dicarboxylic acid content is 30 to 80 % by weight. The glycol content is preferably 30 to 60 % by weight, and the aliphatic dicarboxylic acid content is preferably 40 to 70 % by weight. If the glycol content is less than 20 % by weight the biodegradability is reduced, and if the glycol content exceeds 70 % by weight the strength is reduced. A commercially available example of the glycol/aliphatic dicarboxylic acid is Bionolle (manufactured by Showa Highpolymer).

[0009] The polycaprolactone (which is one of the biodegradable polymers used in the present invention) is a crystalline thermoplastic expressed by the following general formula.

[Chemical Formula 2]



In the formula, *m* is in a range of 0 to 800, and is preferably in a range of 200 to 500; *n* is in a range of 0 to 800, and is preferably in a range of 0 to 300; and *p* is in a range of 0 to 20, and is preferably in a range of 0 to 10. More preferably, the sum of *m*, *n* and *p*, that is to say,

($m + n + p$), is in the range of 300 to 800. The weight-average molecular weight of the polycaprolactone is in the range of 10,000 to 100,000, and is preferably in the range of 20,000 to 80,000. A commercially available example of the polycaprolactone is Placcel (manufactured by Daicel Chemical Industries).

[0010] The biodegradable film provided by the present invention contains two or more biodegradable polymers selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also contains an inorganic filler and an ethylene/vinyl acetate copolymer. In the present invention, when two biodegradable polymers, namely, a lactic acid polymer and a glycol/aliphatic dicarboxylic acid copolymer, are used as a mixture, the polymers are formulated in a weight ratio range of 1/99 to 99/1. A preferred ratio is in a range of 60/40 to 90/10. When another two-type combination of biodegradable polymers, namely, a lactic acid polymer and a polycaprolactone, is used as a mixture, the polymers are formulated in a weight ratio range of 1/99 to 99/1, and preferably in a range of 60/40 to 90/10. When yet another two-type combination of biodegradable polymers, namely, a glycol/aliphatic dicarboxylic acid copolymer and a polycaprolactone, is used as a mixture, the polymers are formulated in a weight ratio range of 20/80 to 80/20, and preferably in a range of 40/60 to 60/40. When three biodegradable polymers, namely, a lactic acid polymer, a glycol/aliphatic dicarboxylic acid copolymer and a polycaprolactone, are used as a mixture, the weight ratio of the glycol/aliphatic acid copolymer to the polycaprolactone is in the range of 30/70 to 70/30, and the weight ratio of the lactic acid to the polycaprolactone is in the range of 20/80 to 80/20.

[0011] Examples of the inorganic filler used in the present invention include silica, talc, calcium carbonate, clay, and alumina, but preferably used among these are silica, talc, and calcium carbonate. The mean particle diameter of inorganic filler used in the present invention is preferably in a range of 1 to 5 μm . If the mean particle diameter is less than 1 μm , sufficient blocking prevention effect cannot be obtained. If the mean particle diameter exceeds 5 μm , the roughness of the film surface after molding increases, and pinholes and other printing nonuniformities occur when images are printed on the film surface; and such a diameter is not preferred. The added amount of the inorganic filler is 0.01 to 5 parts by weight per 100 parts by weight of the biodegradable polymers, and is preferably 0.05 to 2 parts by weight. If the added amount is less than 0.01 parts by weight, sufficient blocking prevention effect cannot be obtained,

and if the added amount exceeds 5 parts by weight, the transparency of the film is reduced; and such added amounts are not preferred.

[0012] The ethylene/vinyl acetate copolymer (EVA) used in the present invention preferably has an ethylene content of 10 to 60 % by weight and a vinyl acetate content of 40 to 90 % by weight. If the vinyl acetate content is less than 40 % by weight, the elongation at break will be low, and if the vinyl acetate content exceeds 90 % by weight, handling is difficult and the Izod impact value will be low, and such a weight is therefore unsuitable for use in film. The average molecular weight is preferably about 50,000 to 500,000. If the molecular weight is less than 50,000, the elongation at break will be reduced, and if it exceeds 500,000, the break strength will decrease. EVA is added in an amount of 5 to 70 parts by weight, but the added amount is preferably 10 to 50 parts by weight with respect to 100 parts by weight of the biodegradable polymers. If the EVA is less than 5 parts by weight, satisfactory elongation at break or impact strength cannot be obtained. If the EVA exceeds 70 parts by weight, the transparency of the present composition will be reduced and the strength will be significantly diminished.

Commercially available examples of EVA include Evathlene 250, 310P, and 450P (manufactured by Dainippon Ink & Chemicals).

[0013] The biodegradable film provided by the present invention contains two or more biodegradable polymers selected from lactic acid polymers, glycol/aliphatic dicarboxylic acid copolymers, and polycaprolactones, and also contains an inorganic filler and an ethylene/vinyl acetate copolymer. The composition may also contain as required one or more components selected from thermal stabilizers, plasticizers, lubricants, and modified silicones.

[0014] The thermal stabilizer used in the present invention may be an inorganic salt of lactic acid, and examples thereof include sodium lactate, barium lactate, calcium lactate, aluminum lactate, magnesium lactate, manganese lactate, iron lactate, zinc lactate, lead lactate, silver lactate, and copper lactate. Preferably used among these are sodium lactate and calcium lactate. One, or two or more of these salts in a mixture may be used. The added amount is preferably in the range of 0.5 to 5 parts by weight, and preferably 1 to 2 parts by weight, per 100 parts by weight of the biodegradable polymers. A thermal stabilizer used in this range improves the impact strength (Izod impact value) and reduces the variability of elongation at break, break strength, and other physical properties.

[0015] Examples of the plasticizer used in the present invention include azelaic acid esters, phthalic acid esters, adipic acid esters, hydroxypolycarboxylic acid esters, and polyester plasticizers. An example of azelaic acid esters is di-2-ethylhexyl azelate (DOZ). Examples of phthalic acid include di-2-ethylhexyl phthalate (DOP), dibutyl phthalate (DBP), and diisodecyl phthalate (DIDP). Examples of adipic acid esters include di-2-ethylhexyl adipate (DOA) and diisodecyl adipate (DIDA). Examples of hydroxy polycarboxylic acid esters include tri-2-ethylhexyl acetylcitrate and tributyl acetylcitrate. Examples of polyester plasticizers include polypropylene glycol adipic acid esters. One, or a mixture of two or more of the above may be used as the plasticizer. Preferably used is di-2-ethylhexyl azelate (DOZ). The added amount of plasticizer is preferably in the range of 5 to 30 parts by weight per 100 parts by weight of the biodegradable polymers. If the added amount is less than 5 parts by weight, the elongation at break and impact strength are reduced, and if the added amount exceeds 30 parts by weight, the break strength and impact strength will be reduced; and such added amounts are not preferred.

[0016] Examples of the lubricant used in the present invention include hydrocarbon resins, fatty acid esters, paraffins, higher fatty acids, and aliphatic ketones, but preferably used among these are hydrocarbon resins, aliphatic esters, and the like. One, or a mixture of two or more of the above may be used. The added amount of lubricant is in the range of 0.05 to 5 parts by weight, and is preferably in the range of 0.5 to 1 part by weight, per 100 parts by weight of the biodegradable polymers. If the added amount is less than 0.05 parts by weight, the effect thereof is inadequate, and if the amount exceeds 5 parts by weight, the resulting film will not wind around a roll, and its physical properties are reduced. Examples of commercially available lubricants include Rikester EW-100 (manufactured by Riken Vitamin), Hoechst Wax OP (manufactured by Hoechst, and carnauba wax (manufactured by Aldrich Chemical).

[0017] Examples of the modified silicone oil used in the present invention include methylstyryl-modified silicone, alkyl-modified silicone, methacrylic acid-modified silicone, polyether-modified silicone, higher fatty acid-modified silicone, and fluorine-modified silicone, but preferably used among these are methylstyryl-modified silicone and alkyl-modified silicone. These silicone oils have a viscosity in the range of 100 to 10,000 cs as measured by Ostwald viscometry at 25°C. If the viscosity is less than 100 cs the resulting film flows more readily and the rolling characteristics worsen, and if the viscosity exceeds 10,000 cs drawbacks arise in the handling characteristics. The silicone oil is added in an amount of 0.05 to 5 parts by weight, and

preferably 1 to 3 parts by weight, per 100 parts by weight of the biodegradable polymers. If the added amount is less than 0.05 parts by weight, a mold release effect cannot be obtained, and if the added amount exceeds 5 parts by weight, the strength is reduced.

[0018] Further description is provided in working examples 1 to 5 and comparative examples 1 and 2. Mixed in the ratios shown in Table 1 were a polylactic acid (ECOPLA, manufactured by Cargill), a glycol/aliphatic dicarboxylic acid copolymer (Bionolle, manufactured by Showa Highpolymer), a polycaprolactone (Placcel, manufactured by Daicel Chemical Industries), silica as the inorganic filler (Aerosil 300, manufactured by Nippon Aerosil), EVA (Evathlene, manufactured by Dainippon Ink & Chemicals), sodium lactate as the thermal stabilizer (manufactured by Wako Pure Chemical Industries), DOZ as the plasticizer (manufactured by New Japan Chemical), aliphatic acid ester as the lubricant (Rikester EW-100, manufactured by Riken Vitamin), and modified silicone oil (KF-410, manufactured by Shin-Etsu Chemical). The resulting blended mixture was kneaded with a 6 inch roll at 140°C for 10 minutes, yielding a molded roll sheet with a thickness of about 1 mm.

[0019] The resulting molded roll sheets were evaluated for mold release properties, tensile strength, and impact strength by using the following tests.

Mold release properties: The ease of peeling from a roll was evaluated with the following criteria when a molded sheet with a thickness of about 1 mm was removed from the 6 inch roll.

- A: very easy to peel
- B: easy to peel
- C: slightly difficult to peel
- X: difficult to peel

Tensile test: The resulting molded roll sheet was cut and press molded at 160°C under a pressure of 50 kgf/cm² for 8 minutes to fabricate flat plate samples with a thickness of 1 mm for the tensile test, and the samples were subjected to the tensile test according to JIS K-7113.

Izod impact test: The resulting molded roll sheet was cut and four cut samples were superimposed and press molded at 160°C under an actual pressure of 50 kgf/cm² for 10 minutes to fabricate flat plate samples with a thickness of 3 mm for the Izod impact test. The samples were tested with the Izod impact test in accordance with JIS K-7110.

[0020] The resulting molded roll sheet was pelletized with a pelletizer. The pellets were extrusion molded under the conditions shown below using a 20-mm diameter extruder, yielding an extrusion molded sheet with a thickness of 0.2 mm.

20-mm diameter extrusion conditions:

Cylinder temperature: $C_1 = 120^\circ\text{C}$, $C_2 = 145^\circ\text{C}$, $C_3 = 160^\circ\text{C}$

Die temperature: $D = 177^\circ\text{C}$

Screw: CR = 1.0

Screw speed: 30 rpm

The resulting extrusion molded sheet was drawn 400% at 65°C in the width direction using a drawing machine to fabricate a drawn film with a thickness of 0.05 mm.

[0021] The resulting molded roll sheet was evaluated for transparency with the following method and the blocking prevention characteristic was evaluated

Transparency evaluation: The transparency of the drawn film with a thickness of 0.05 mm was evaluated in accordance with the following criteria.

A: Transparent with no clouding

X: Turbidly transparent with clouding

Evaluation of blocking prevention characteristics: The resulting drawn film with a thickness of 0.05 mm was cut to a size of (lengthwise 10 cm) \times (crosswise 10 cm) and 10 samples were superimposed to fabricate a sample. The superimposed sample was placed in the thermostat with the temperature and humidity adjusted to 30°C and 60% RH, and left to stand under pressure for one week in an atmosphere of 30°C and 60% RH under a load of 20 gf/cm^2 . The 10-layer sample was removed from the thermostat after one week and the blocking prevention effect was evaluated in accordance with the following criteria.

A: The film layers do not adhere to each other, the film does not need to be separated one layer at a time, and the film layers separate smoothly from each other.

X: The film layers adhere to each other and each film layer needs to be peeled away one layer at a time.

[0022]

[Table 1]

| | Working Example 1 | Working Example 2 | Working Example 3 | Working Example 4 | Working Example 5 | Comparative Example 1 | Comparative Example 2 |
|--|-------------------|-------------------|-------------------|-------------------|-------------------|-----------------------|-----------------------|
| Blend ratio (parts by weight) | Polylactic acid | 100 | 100 | 100 | 0 | 100 | 100 |
| | Bionolle | 40 | 0 | 20 | 50 | 0 | 40 |
| | Polycaprolactone | 0 | 40 | 20 | 50 | 10 | 0 |
| | Silica | 0.5 | 0.5 | 0.5 | 0.5 | 0 | 0 |
| | EVA | 40 | 40 | 40 | 40 | 20 | 40 |
| | Sodium lactate | 0 | 0 | 0 | 0 | 1.0 | 0 |
| | DOZ | 0 | 0 | 0 | 0 | 10.0 | 0 |
| | Rikester EW-100 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0 |
| | KF-410 | 0 | 0 | 0 | 0 | 1.0 | 0 |
| Evaluation of mold release properties | A | A | A | A | B | B | X |
| Tensile test | | | | | | | |
| Yield strength (kgf/mm ²) | 4.4 | 3.0 | 3.6 | 3.5 | 3.5 | 3.5 | 4.2 |
| Break strength (kgf/mm ²) | 3.1 | 2.8 | 3.0 | 3.2 | 3.2 | 3.2 | 4.1 |
| Elongation at break (%) | 210 | 137 | 95 | 125 | 145 | 125 | 4.4 |
| Izod impact strength (kgf·cm/cm ²) | 40 | 18 | 41 | 24 | 20 | 24 | 23 |
| Transparency evaluation | A | A | A | A | A | A | A |
| Blocking prevention evaluation | A | A | A | A | A | X | X |

Polylactic acid: ECOPLA (manufactured by Cargill) with a weight-average molecular weight of 168,300

Bionolle: glycol/aliphatic dicarboxylic acid copolymer, Bionolle #1010 (manufactured by Showa Highpolymer) with a glycol content of 40 % by weight, an aliphatic dicarboxylic acid content of 60 % by weight, and a weight-average molecular weight of 69,300

Polycaprolactone: Placcel (manufactured by Daicel Chemical Industries) with a weight-average molecular weight of 45,200

Silica: Inorganic filler, Aerosil 300 (manufactured by Nippon Aerosil) with a mean particle diameter of 2 µm

EVA: Evathlene 450P (manufactured by Dainippon Ink & Chemicals) with an ethylene content of 20 % by weight, a vinyl acetate content of 80 % by weight, and a weight-average molecular weight of 248,000

Sodium lactate: thermal stabilizer (manufactured by WAKO Pure Chemical Industries)
DOZ: plasticizer composed of di-2-ethylhexyl azelate (manufactured by New Japan Chemical)
Rikester EW-100: lubricant composed of an aliphatic acid ester (manufactured by Riken
Vitamin)
KF-410: methylstyryl-modified silicone oil (manufactured by Shin-Etsu Chemical) with a
viscosity of 1,000 cs at 25°C.

[0023]

[Effect of the Invention] It is apparent from Table 1 that the present invention provides a biodegradable film with sufficient blocking prevention effect, and excellent mold release properties, elongation at break, Izod impact strength, and transparency. The present film possesses excellent printability, and pinholes and other printing nonuniformities do not occur when images are printed on the surface of the film.

(Continued from front page)

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